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Features of Technogenic Iron Oxide Recovery

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Abstract. The overview of existing models for iron oxides reducing and an analysis of their applicability to technogenic formations is presented. The thermodynamic analysis data of iron oxides reducing reactions through solid and gas phases and experiment results presenting features of technogenic iron oxide reducing under conditions of solid-phase diffusion (limited diffusion) and partially liquid-phase diffusion (easier diffusion) of iron oxide ions. It is shown that under conditions of iron oxide ions solid-phase diffusion the reduction processes rate is significantly affected by the briquetting pressure, which increases the contact area of reacting substances. The briquetting pressure does not affect the reduction processes rate under conditions of partially liquid-phase diffusion of iron oxide ions. An ion-diffusion catalytic mechanism is proposed to describe the observed effects of technogenic iron oxide reducing.

1. Introduction

A huge number of technogenic formations that accumulated by metallurgical plants is a source of environmental pollution. At the same time, it is also a promising stock of raw materials, of which iron is the most valuable for ferrous metallurgy. Technogenic formation of the iron oxide presented mostly by sludge and scale. In such technogenic formations all iron oxides can be present simultaneously, and they are arranged in layers in the scale. The layered structure of the scale is completely consistent with the diagram of the iron-oxygen state. Above the temperature of 650 °C, the inner layer of scale consists of wustite (FeO), the middle layer of magnetite (Fe₃O₄), and the outer layer of hematite (Fe₂O₃) [1].

Wustite (FeO) is a thermodynamically unstable compound, below the temperature of 560 °C, it decays into α -Fe and magnetite (Fe₃O₄). The crystal lattice is cubic, $a = 4.29$ Å. The wustite crystal lattice always contains an excess of oxygen, so its composition corresponds more precisely to the non-stoichiometric formula Fe_{0.91}O or FeO_{1.09}. As a result of this, the wustite crystal lattice contains a significant number of non-stoichiometry defects in the form of Fe²⁺ ion vacancies [2]. From a structural point of view, wustite refers to subtraction solid solutions: in its lattice, oxygen atoms occupy all the nodes in the anionic sublattice, and some nodes in the cationic sublattice are not occupied by iron ions. If there is a lack of Fe²⁺ cations in the lattice, its electroneutrality is



maintained due to the conversion of part of Fe^{2+} cations to Fe^{3+} , so this non-stoichiometric compound can be considered as a substitution solid solution of Fe_2O_3 in FeO [3].

Iron oxide $\alpha\text{-Fe}_2\text{O}_3$ (hematite) is characterized by a rhombohedral corundum-type lattice with parameters $a = 5.42 \text{ \AA}$ and $\alpha = 55^\circ 17'$. The unit cell of hematite is formed by four Fe^{3+} and six O^{2-} ions, which form a dense hexagonal package. One-third of the octahedral voids are vacant, and two-thirds of them are filled with Fe^{3+} [2].

Magnetite (Fe_3O_4) has a cubic lattice of “reversed” spinel with $a = 8.38 \text{ \AA}$. 8Fe^{2+} , 16Fe^{3+} and 32O^{2-} are present in the unit cell of magnetite. Oxygen ions form a dense cubic lattice containing 32 octahedral and 64 tetrahedral voids in one unit cell. In this case, eight Fe^{2+} and the same amount of Fe^{3+} are distributed (statistically) in octahedral, and the remaining eight Fe^{3+} – in tetrahedral internodes. The presence of Fe^{2+} and Fe^{3+} in the same crystallographic positions (octahedral) facilitates the exchange of electrons and makes magnetite highly conductive [2].

Decomposition of iron oxides occurs due to the influence of gaseous or solid reducing agents. The most important reducing agent of iron, widely used in metallurgical practice, is carbon. Several models have been proposed to describe the mechanism of metal oxides reduction by carbon [4–8]. S. I. Popel and his colleagues proposed 4 recovery schemes [9]. The first scheme is based on the most frequently used two-stage recovery scheme based on the adsorption-catalytic mechanism of G. I. Chufarov [10].

According to the first scheme, it is assumed that the process is carried out as a result of two simultaneous reactions:

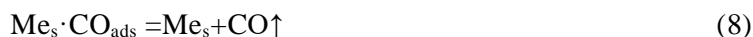


The reduction of iron oxide in this scheme occurs through CO, and the role of solid carbon is reduced to the regeneration of carbon oxide by the Bell-Boudoir reaction.

According to the second (dissociative) scheme, the reduction of metals with a sufficiently high dissociation elasticity ($-\Delta p^\circ_{\text{O}_2} \geq 1 \text{ Pa}$) can proceed by dissociation of the oxide and subsequent interaction of molecular oxygen with carbon:



According to the third scheme, if the reduction and sublimation temperatures of the oxide are close, the interaction of the oxide and the reducing agent is possible due to the evaporation of the oxide with subsequent condensation (adsorption) of its vapors on the carbon surface, where the reduction process occurs:



In this way, it is possible to reduce the volatile oxides of MoO_3 , WO_3 , Nb_2O_5 , etc.

According to the fourth scheme, the reduction occurs directly during contact of solid phases - the interaction of solid carbon and oxide. This is one of limiting factors in the scheme implementation. At the beginning, this contact is direct, and after formation of separating layer of metal or lower oxide, it is carried out by the diffusion of reagents through this layer. According to the authors [9], the flow of the 4 scheme is very possible, but its contribution to the overall kinetics of metals direct reduction from oxides is negligible, since the actual particles contact surface is an insignificant fraction of their total surface. The second limiting factor of the fourth scheme possibility is the diffusion of reagents, which is quite slow at low temperatures.

According to [11], all the described schemes are based on outdated provisions of the atomic-molecular theory of reduction, which represents atoms as solid indivisible balls, and do not take into account advances in the study of the fine structure of matter and physical theories describing the behavior of elementary particles that make up atoms.

2. Thermodynamic analysis of the reactions of reduction of iron oxides

The total reaction of all four schemes is the reaction (9):



In relation to a specific iron oxide, this interaction is possible by the following reactions (10–12):



Reduction of specific iron oxides through the gas phase is possible by reactions (13–15):



According to [11], when cementite is formed in the system by reaction (16):



it is also possible to reduce iron through the gas phase by reaction (17)



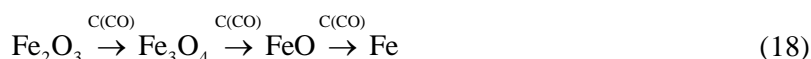
Thermodynamic calculations were performed to determine the temperature range in which the reduction reactions of specific iron oxides can occur through the solid and gas phase. The results of calculating the Gibbs free energy for reactions (10–17) are shown in table 1.

Table 1. Value of Gibbs free energy of iron oxide reduction reactions.

Reaction №	ΔG_T^0 , J/mol, at temperature, °C					
	500	600	700	800	900	1000
10	151.2	47.3	-55.6	-158.0	-260.4	-362.5
11	136.9	71.1	6.0	-58.9	-123.9	-188.8
12	33.7	18.3	2.9	-12.5	-27.9	-43.3
13	-30.3	-29.2	-27.7	-26.5	-25.4	-24.5
14	-1.0	0.2	1.4	2.6	3.8	4.8
15	-1.6	0.7	2.9	5.0	7.0	8.9
16	26.3	15.6	5.0	-5.4	-15.7	-25.8
17	6.8	3.2	-0.4	-4.1	-7.9	-11.9

According to the data presented in table 1, reduction of Fe_2O_3 oxide (reaction 10) by direct interaction of solid phases is thermodynamically possible starting from the temperature of 700 °C, and Fe_3O_4 and FeO (reactions 11 and 12) – starting from the temperature of 800 °C. Through the gas phase, reduction of Fe_2O_3 (reaction 13) is possible in the entire temperature range (from room

temperature to 1000 °C). Above the temperature of 600 °C, recovery through the gas phase of Fe₃O₄ and FeO (reactions 14 and 15) is thermodynamically impossible. Since in accordance with the principle of sequence of transformations formulated by A. A. Baikov [12] above the temperature of 570 °C, the transition from higher iron oxides to lower ones proceeds according to the scheme:



And according to the data [13] given in table 2, the content of Fe₂O₃ in the scale at a temperature above 700 °C is insignificant, so it is very likely that above this temperature the reduction of Fe₃O₄ and FeO occurs only with the participation of solid carbon in the reactions (11) and (12). Above the temperature of 700 °C through the gas phase, it is also possible to restore iron by reaction (17), but this will only happen if cementite is formed in the system by reaction (16).

Table 2. The content of iron oxides in the slag at elevated temperatures.

Temperature, °C	Scale oxide content, mass. %		
	FeO	Fe ₃ O ₄	Fe ₂ O ₃
600	50	50	0
700	98	2	0
800	96	2	2
900	90	9	1
1000	95	4	1
1090	94	5	1

Since above the temperature of 700 °C for Fe₂O₃, and for Fe₃O₄ and FeO above 800 °C, the reduction reaction is thermodynamically possible through the solid phase, it is difficult to explain the high rate of iron oxides reduction under conditions of practically no diffusion of reagents in the solid phase using the provisions of the classical atomic-molecular theory of reduction.

Under these conditions, there are only two ways to accelerate the reduction of iron oxides with carbon:

- 1-in the absence of diffusion of reagents, increase the area and number of their contacts;
- 2-create conditions for favorable diffusion of reagents.

According to [14, 15], the area and number of contacts of reacting solid phases can be increased by their joint grinding and subsequent pressing. In [16], same approach was used in the example of the synthesis of nickel ferrite, zincaluminates and magnesium aluminates from oxides under pressure from atmospheric to 60 kbar. The observed strong acceleration of these reactions is explained by an increase in the contact area of the reacting particles and, thus, an improvement in the conditions for diffusion along the interphase surfaces.

The diffusion rate of reactants can be increased by partial destruction of their crystal lattice. This is possible due to the fluxes introduction into the mixture of scale and carbon, which reduce the melting point of the scale, lead to the formation of local liquid-phase zones, in which the diffusion rate of reacting substances increases by several orders.

3. Experimental method

The rolling scale was used in this work. According to the phase analysis results, the scale contained, mass. %: 43.4 FeO, 27.0 Fe₃O₄ and 29.6 Fe₂O₃, with a Fe_{all} content of 73.4. The coke was used as a reducing agent with a carbon content of 92mass.%. Its amount was 15% over the stoichiometric ratio. To assess the iron oxides reduction rate, in the absence of reactants diffusion,

the raw mixture was prepared only from scale and coke. To assess the iron oxides reduction rate, under conditions of easier diffusion of reacting substances, a flux based on CaO, MgO, SiO₂, Al₂O₃, Na₂O and CaF₂ was added to the scale and coke mix in an amount of 10% of the mass of the scale. Scale, coke and flux were dried to a constant mass and joint grinded to a specific surface area by Blain≈400 m²/kg. The material mixture of scale, reducing agent and flux prepared in this way was pressed at pressures of 100, 200 and 300 MPa.

Heat treatment of the pressed raw material mixture was carried out in an argon atmosphere with the removal of gas reaction products. Heating was performed to a temperature of 1200 °C. The thermal characteristics of the raw material mixture were determined during the heating process, and the phase composition of the heating products was determined. Qualitative x-ray phase analysis was performed using an XRD-7000 diffractometer (Shimadzu). Quantitative x-ray phase analysis was performed using a STADI-P diffractometer (STOE, Germany). The survey was performed in CuKα-radiation (40 kV, 30 mA), graphite monochromator, in the range of scattering angles 2Θ = 10 – 70 degree, with a step of 0.02 degree. The results were analyzed using the PDF-2 database (Release 2008 RDB 2.0804). Thermal analysis (TA) was performed using the DSC method (differential scanning calorimetry) on the STA 449 F3 Jupiter thermal analyzer (Netzsch-Geratebau GmbH). The experiment was conducted in an argon atmosphere (Ar 99.998 %), under the condition of linear heating at a speed of 10 °/min, the temperature measurement error is no more than ± 1.5 degree. Al₂O₃ crucibles with lids were used for the study. The value of the endothermic effect was calculated in the software module of the device in J/g and converted to kJ/mol by multiplying the data of the device by the mole mass of metallic iron.

4. Results

Figure 1 shows the TA data of the material mixture without the flux addition. Presented data shows, that starting from a temperature of about 300 °C, the DSC curves are separated strictly according to the pressure during pressing. The line for not pressed scale is the upper, and the line for scale, pressed at 300 MPa, is the low. This indicates the pressing limiting influence on the process of studied mixture thermodynamic state converting. Due to a more dense contact of the reacting phases, provided by increasing pressing pressure, the thermodynamic state of the mixture changes at the expense of less heat. At a temperature of about 600 °C, a small endothermic effect is observed. It indicates the beginning of the Fe₂O₃ reduction process, according to reaction 19, which is the first stage of the proposed scale reduction mechanism described below. According to thermodynamic calculations, this reaction is possible starting from the temperature of 539 °C.



Upon further heating at a temperature of about 1000 °C, a small endothermic effect is observed in the non-pressed and pressed scale at 100 MPa, indicating the end of the reducing process of Fe₂O₃ to Fe₃O₄ by reaction 20 and reducing of Fe₃O₄ to FeO by reaction 21.



Reactions 21 and 22 are the second stage of the proposed scale reduction mechanism described below. The scale pressed at 200 and 300 MPa has no small endothermic effect, due to the increasing in pressing pressure accelerate the recovery processes, and all hematite is reduced at the first stage. That is confirmed by the data of the phase analysis described below. Figure 2 shows the effect of pressing pressure on the temperature of metallic iron formation beginning from a mixture without flux.

In accordance with Figure 2 when the pressing pressure increases, the metallization beginning shifts to the lower temperature range from 1021.7 °C at 0 MPa to 989.8 °C at 300 MPa.

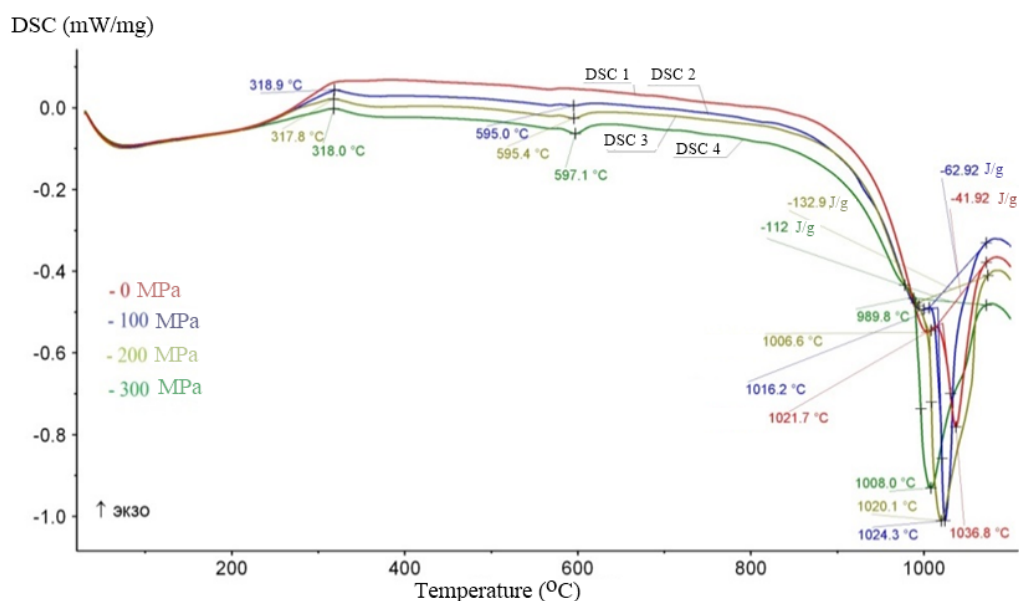


Figure 1. DSC data from of the pressed material mixture of rolled scale and coke without the flux.

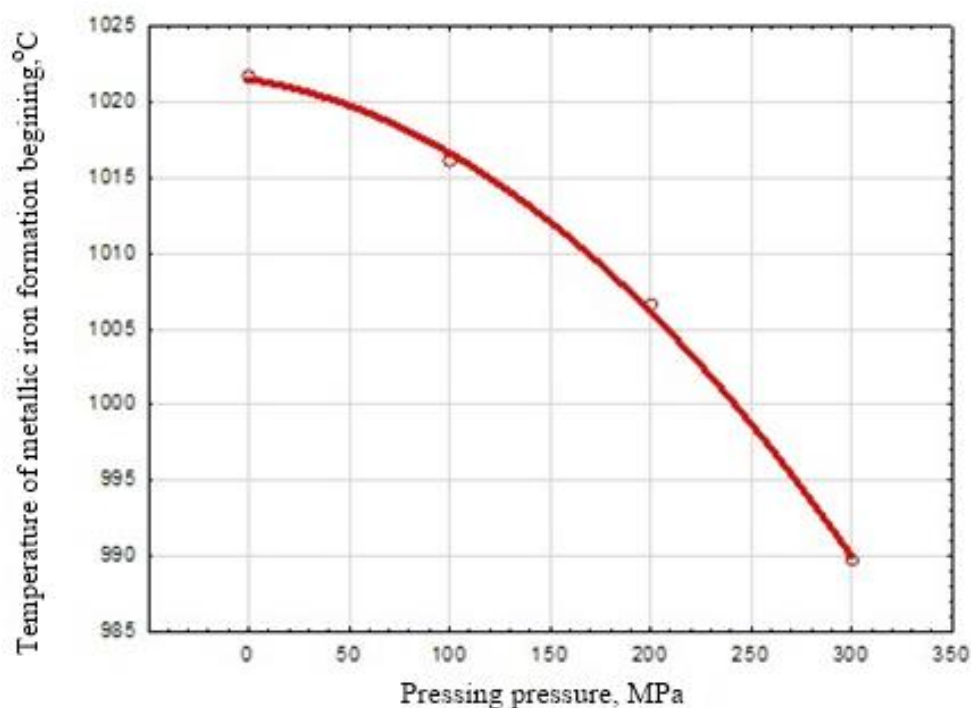


Figure 2. Influence of pressing pressure on the temperature of metallic iron formation beginning from a mixture without flux.

As the pressing pressure increases, the enthalpy of metallic iron formation and the degree of metallization also increases. The change of these parameters depending on the pressing pressure is shown in figure 3. The enthalpy of iron metal formation increases from 2.3 kJ/mol at 0 MPa to 6.6 kJ at 300 MPa. The metallization degree increases from 34.0 % to 72 %, respectively. The data of

comparative qualitative phase analysis of the pressed mixture without flux, heated in an argon atmosphere, is shown in Figure 4. Figure 5 shows the change in the heating products phase composition of the mixture without flux, depending on the pressing pressure according to quantitative phase analysis.

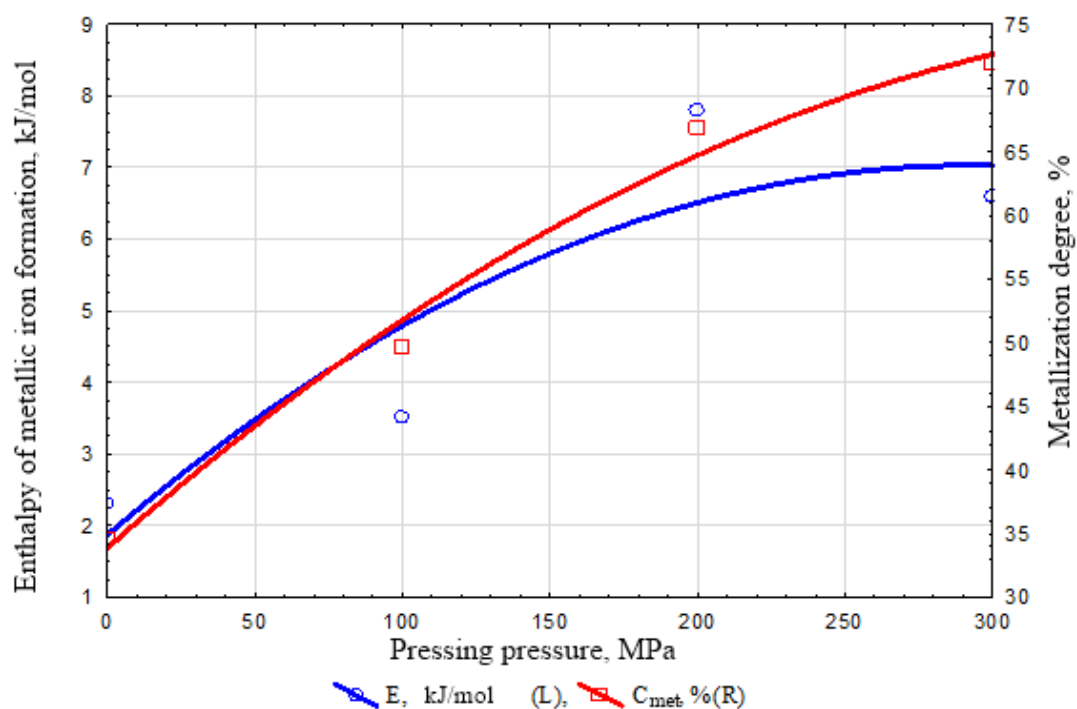


Figure 3. Influence of pressing pressure on the metal iron formation enthalpy and on the mixture without flux metallization degree.

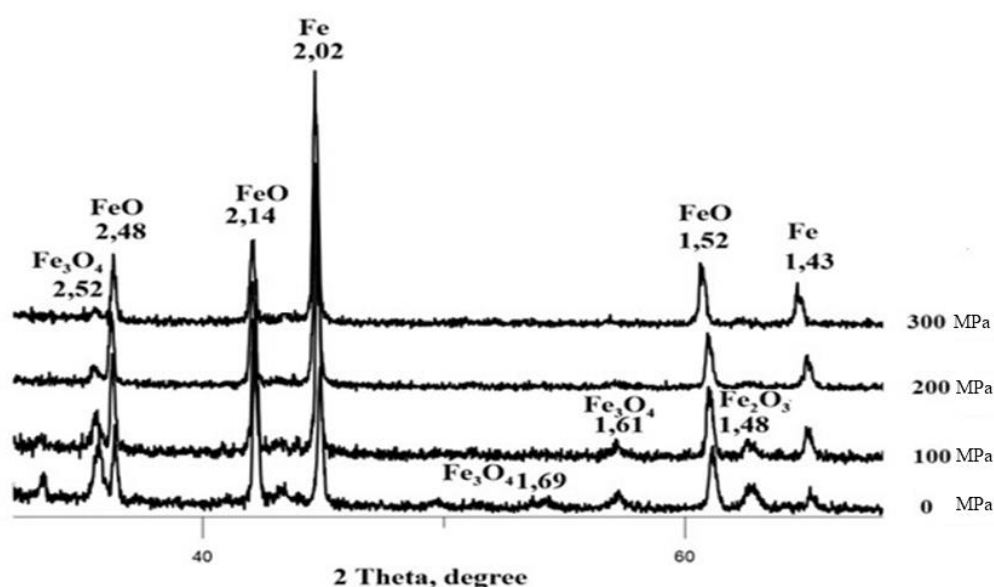


Figure 4. Influence of the pressing pressure of a raw mixture without flux heated in an argon medium on the change in its phase composition.

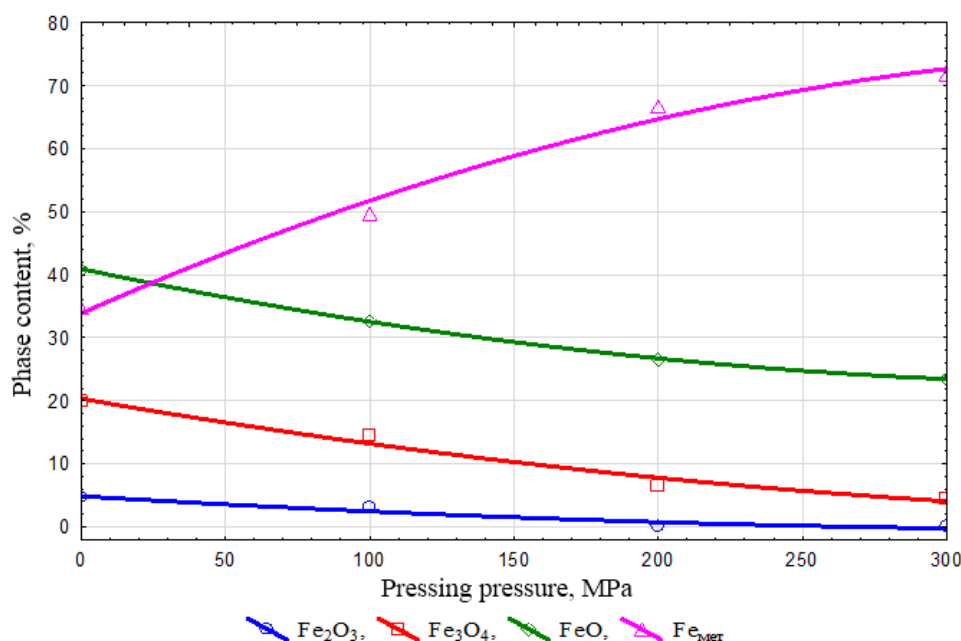


Figure 5. Influence of the pressing pressure of the raw material mixture without flux on the change in the phase composition of heating products according to quantitative phase analysis.

According to quantitative phase analysis, the residual content of Fe₂O₃ in the heating products of non-pressed scale and pressed at 100 MPa is 4.6 and 3.2 %, respectively. There is no Fe₂O₃ in the heating products of scale pressed at 200 and 300 MPa. Thus, the phase data confirm the conclusions made after DSC analysis, that a small endothermic effect at a temperature of 1000 °C indicates the completion of the reducing process of Fe₂O₃ to Fe₃O₄. In addition, from the phase analysis data, it follows that under the same conditions of heat treatment, with an increase in the pressing pressure, the content of iron oxide phases decreases from 65.4 % for non-pressed scale to 28.0% for scale pressed at 300 MPa. The content of metallic iron, on the contrary, increases.

Figure 6 presents TA data of pressed mixture with 10 % flux.

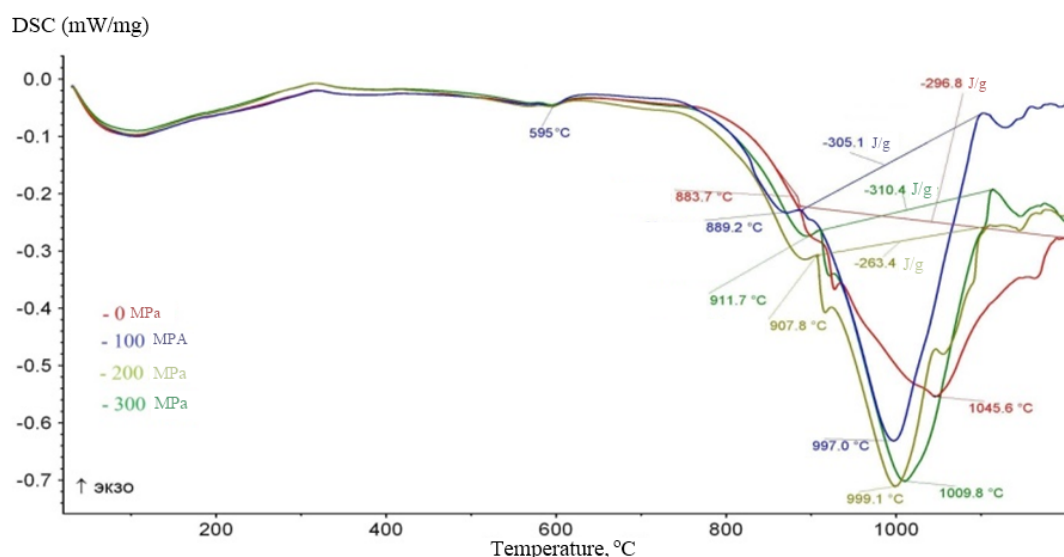


Figure 6. DSC data of the pressed mixture of scale and coke with the addition of 10% flux.

The data presented in Figure 6 show that, at a temperature of 600 °C, all four compositions have a small endothermic effect, and the separation of the DSC curves depending on the pressing pressure also begins at this temperature. Small endothermic effects at a temperature of 1000 °C are observed in all compositions. Figure 7 shows the effect of pressing pressure on the metallic iron formation beginning temperature for the mixture with the flux.

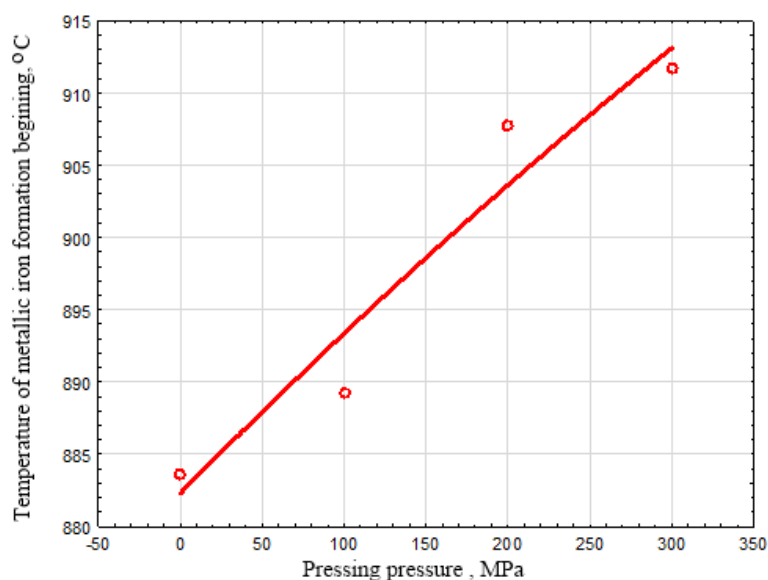


Figure 7. Influence of pressing pressure on the temperature metallic iron formation beginning temperature for the mixture with the flux.

In accordance with figure 7, the material mixture with the flux has the temperature of the metallic iron formation beginning shifted to the higher temperatures from 883.7°C at 0 MPa to 911.7°C at 300 MPa.

Figure 8 shows the pressing pressure effect on the change in the metallic iron formation enthalpy and the metallization degree of the mixture with the flux.

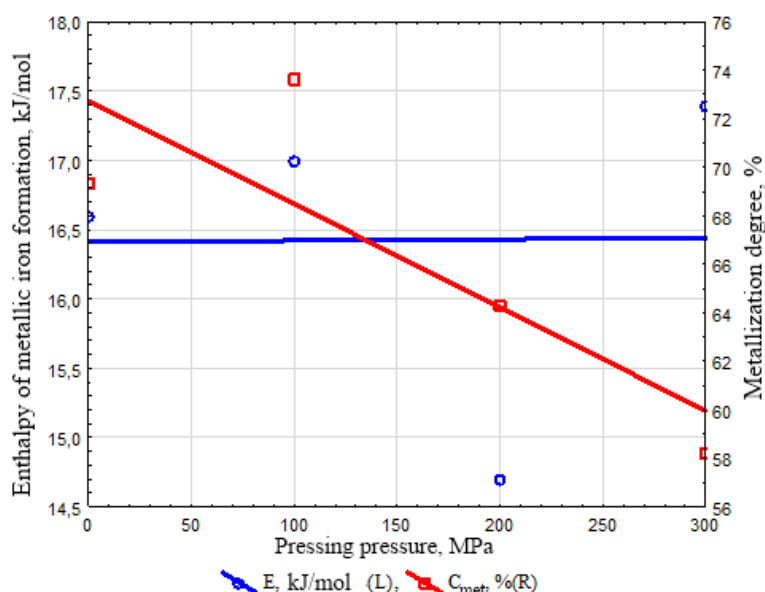


Figure 8. The pressing pressure effect on the change in the metallic iron formation enthalpy and the metallization degree of the mixture with the flux.

According to the figure 8, it can be seen that in the mixture containing flux, with increasing pressing pressure, the metal iron formation enthalpy increases slightly from 16.6 kJ/mol at 0 MPa to 17.4 kJ/mol at 300 MPa, and the metallization degree even slightly decreases, respectively, from 69.3 % to 58.2 %. The data of comparative qualitative phase analysis of the pressed material mixture with 10 % flux, during heating in an argon atmosphere, are shown in figure 9.

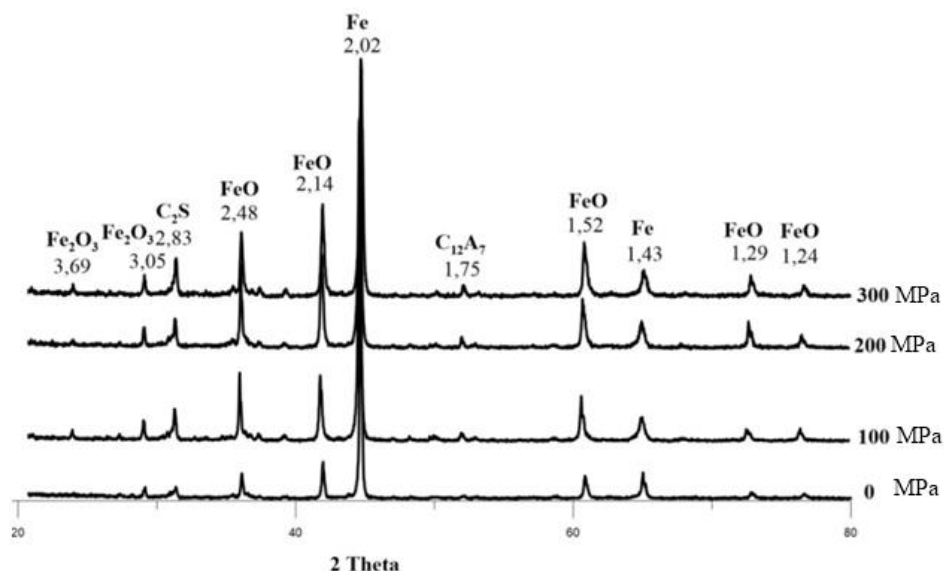


Figure 9. Pressing pressure of the materials mixture containing flux effect on its phase composition change, during heating in an argon atmosphere.

Figure 10 shows the firing products phase composition change depending on the pressing pressure of the mixture containing flux according to quantitative phase analysis.

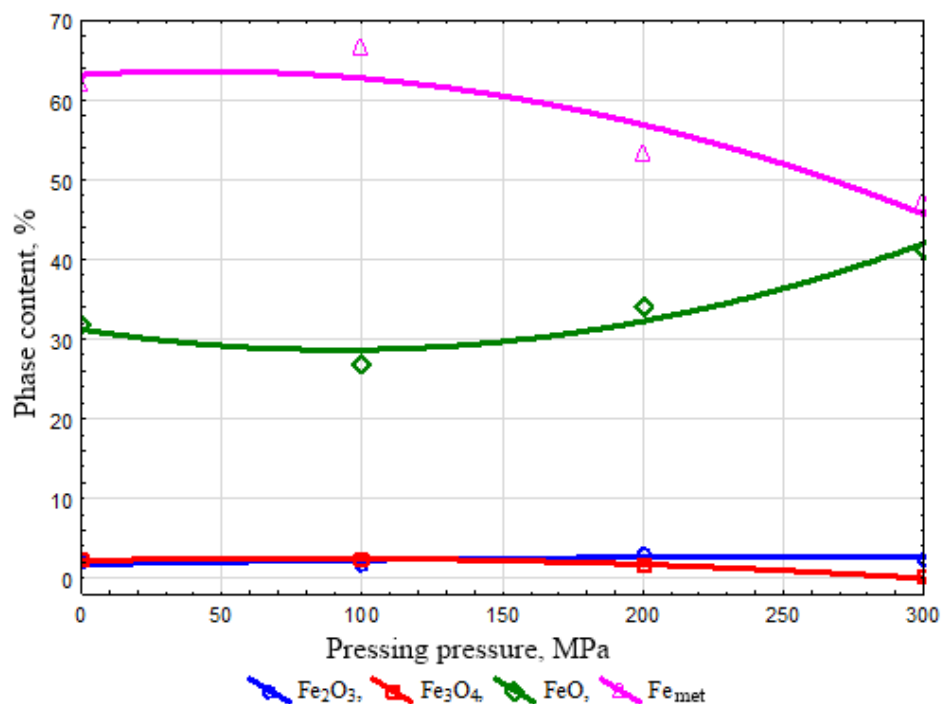


Figure 10. Pressing pressure of a mixture containing flux effect on the heating products phase composition change according to quantitative phase analysis.

The phase analysis data shown in figure 9 and 10 show a small content of hematite and magnetite in the heating products of the mixture containing flux, and it practically does not change with increasing pressing pressure. The FeO content increases with increasing pressing pressure from 31.8 % for non-pressed to 41.4 % for pressed at 300 MPa scale, and the content of metallic iron, on the contrary, decreases from 69.3 % to 46.9 %, respectively.

According to the data presented in figure 7, 8 and 10, it can be seen that the pressing pressure does not significantly affect the measured parameters when the material mixture contains 10% of flux, in contrast to the material mixture that does not contain flux.

5. Discussion

The results of thermodynamic analysis show that the recovery of hematite, magnetite and vustite above the temperature of 700 °C is possible through solid-phase interaction of reagents. Roasting of the mixture based on coke and scale in an argon atmosphere with the gaseous products removing from the reaction zone, i.e. in conditions that exclude the participation of gaseous products in the recovery process, showed that the recovery processes are successfully implemented with a high degree of metallization through the solid phase.

It is hard to explain the observed effects from the classical atomic-molecular theory of reduction point of view. That theory determine that the reacting substances atoms difficult diffusion in the solid phase cannot provide a high rate of the reduction processes. Observed effects can be explained by the theory presented by V. E. Roshchin and colleagues about the role of electronic processes in the iron oxides reduction [17–21]. To explain the observed effects, we propose an ion-diffusion-catalytic mechanism for iron oxides solid-phase reduction, which details statements of V. E. Roshchin's theory in relation to iron oxides of technogenic origin.

According to this mechanism, at the first stage, the solid-phase interaction of the hematite located on the surface of the scale with the solid carbon located in the intergranular space occurs, with the formation of a CO by reaction (19). As indicated above, this reaction is possible starting from the temperature of 539 °C. The endothermic effect observed on the DSC curves at a temperature of ≈ 600 °C corresponds to the beginning of the recovery first stage. In accordance with the statements of Roshchin's theory the metallic iron crystal lattice is a crystal structure with cations at its nodes, and collectivized valence electrons fill the space between the cations and bind them to the backbone of the crystal lattice. When metal iron is oxidized, oxygen dissolves in it and adds its electronic shell with valence electrons, becoming an anion. The metal is transformed into a higher oxide after all collectivized electrons becomes binded with anions. During reducing, reverse processes occur. Oxygen does not carry away the previously captured valence electrons when extracted from the scale surface due to inter-grain carbon interaction, since this would disrupt the charges balance in the oxide. In our opinion, it transfers electrons to neighboring iron cations. As a result, an oxygen vacuum is formed on the scale surface, two atoms of divalent iron and, respectively, two molecules of vustite.

Resulting vustite molecules are thermodynamically unstable, since they are thermodynamically predisposed to interact with the below hematite layers to form two magnetite molecules by the reaction (20), which is the beginning of the recovery second stage. At 600 °C, the Gibbs free energy of this reaction is -58.4 kJ/mol. The end of the recovery second stage is the interaction of oxygen of newly formed magnetite molecules with solid intergranular carbon, with the formation of 6 FeO and CO molecules by reaction (21). Small endothermic effects of ≈ 1000 °C correspond to the curves of this reaction, and they are observed only in mixtures with a sufficient amount of residual Fe_2O_3 . The reaction (21) is thermodynamically possible starting from a temperature of 700 °C. As a result of this reaction, oxygen will transfer electrons to neighboring iron atoms with the formation of 6 divalent iron atoms (6 vustite molecules, respectively) and the formation of 2 oxygen vacancies. The newly formed vustite molecules also will be associated with the remaining neighboring hematite molecules with the formation of magnetite molecules. Due to the formation of a vustite molecules significant number, the catalytic acceleration of the scale reduction processes will occur with the promotion of divalent iron ions deep into the scale, and oxygen anions to the surface, in the direction of oxygen vacancies. Due to

the catalytic acceleration, provided by the vustite significant amount formation, at the third stage of reducing process, it is restored to metallic iron. At the final stage, only vustite molecules and oxygen vacancies will be located on the scale surface. The vustite oxygen interaction with solid carbon will lead to the metallic iron and CO formation by reaction (12). According to thermodynamic calculations (table 1), this reaction is possible from the temperature of 800 °C, and a large endothermic effect in the phase of the highest reaction speed corresponds to this reaction on all DSC curves. During the third stage, oxygen anions will move to the surface, and the cations of metallic iron formed during this process will form an apparent flow of movement into the crystal.

The test results show that without the introduction of flux into the material mixture, the pressing pressure has a significant effect on the firing products phase composition and the recovery process parameters. When the material mixture contains 10 % flux, the pressing pressure effect on the firing products phase composition and the recovery process parameters is minimal. These data indicate that when a sufficient amount of flux is introduced into mixture, the diffusion processes begin to prevail over the dense packing processes associated with pressing pressure. In other words, a introduced flux sufficient mass eliminates a diffusion difficulties significant part in the process mechanism, ensuring that the metallization beginning temperature is close to the minimum limit (due to thermodynamics). Also, we can say that the introduction of flux and pressing to some extent have an equivalent effect associated with an increase in the mobility of ions and the growth of the grains active surface.

6. Conclusions

1. Data of thermodynamic calculations and experimental data are presented. Results can be explained by the solid-phase interaction of scale iron oxides and carbon.
2. To describe observed effects, an ion-diffusion-catalytic mechanism for scale iron oxides solid-phase reduction is proposed, which details and clarifies the statements of the V. E. Roshchin and colleagues theory in relation to iron oxides of technogenic origin.

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